

ARMY RESEARCH LABORATORY



Investigation of Possible Decomposition of Alternative Fire-Extinguishing Agents Discharged Through a Vehicle Personnel Heater

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13. ABSTRACT (Maximum 200 words) Fourier transform infrared (FT-IR) spectroscopy was used to monitor the possible thermal decomposition of alternative fire-extinguishing agents discharged through a vehicle personnel heater. The agent was introduced into the heater air induction port and flowed across the heat exchanger manifold. Gas samples were removed from the hot air output duct extension of the heater via stainless steel tubing and flowed through a 10-m path-length multipass optical gas cell placed in the sample beam of an FT-IR spectrometer. Five fire-extinguishing agents, CF ₃ Br (trade name, Halon 1301), C ₃ F ₇ H (FM-200), C ₃ F ₆ H ₂ (FE-36), C ₂ F ₅ H (FE-25), and CF ₃ H (FE-13), were tested for two manifold temperatures of 380 and 480–510° C. No agent decomposition or combustion gas products could be detected for any of the agents tested under these temperature conditions. The agent decomposition products of interest were HF, HBr, CO, CF ₃ H, C ₂ H ₂ , CH ₄ , C ₂ H ₄ , and CF ₂ O.				
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1. INTRODUCTION

The cessation of the production and sale of ozone-depleting halogenated hydrocarbons (halons) (e.g., CF_3Br - Halon 1301) has increased the effort of finding suitable replacements (Wray 1992; Philipczak 1993). However, researchers face formidable obstacles in developing a product that equals the firefighting capabilities of halons. Among the main criteria for the suitability of a halon alternative are: (1) it must be as effective at extinguishing fires as those agents it replaces, (2) it must be economically viable, (3) its ozone-depletion factor should be lower than 0.2, the level that must be met by the year 2000 under current proposed regulations (halons have ozone-depletion factors ranging from 3 to 10) (Federal Register 1992), and (4) human tolerance for the chemical must be high for the conditions where it is employed.

Recently, this laboratory reported the results of a Fourier transform infrared (FT-IR) spectroscopic investigation of the toxic gases produced during the inhibition of JP-8 fuel fires by CF_3Br (Halon 1301) and $\text{C}_3\text{F}_7\text{H}$ (FM-200) (Modiano et al., to be published). It was shown that, in JP-8 fires inhibited by either agent, toxic gas products were generated that pose serious health risks to the personnel exposed to the combustion gases. For each agent tested, the principal toxic gases produced during inhibition of JP-8 fires were CF_2O and HF. For JP-8 fires inhibited by CF_3Br , a surprising high level of HBr was also produced.

The current work continues the investigation of the potential toxic decomposition and combustion products formed during the application of fire-extinguishing agents under specific working conditions. There had been concern that military vehicles equipped with fuel-fired personnel heaters are capable of producing toxic gases when fire-extinguishing agents are flowed across the hot heat exchanger manifold of the heater. FT-IR absorption spectroscopy was used to measure spectra of gases removed from the hot air output duct of the heater, while the fire-extinguishing agent was introduced into the heater air induction port. Five fire-extinguishing agents were tested: Halon 1301 (CF_3Br), FE-25 ($\text{C}_2\text{F}_5\text{H}$), FM-200 ($\text{C}_3\text{F}_7\text{H}$), FE-13 (CF_3H), and FE-36 ($\text{C}_3\text{F}_6\text{H}_2$).

2. EXPERIMENTAL

The schematic diagram representing the experimental setup is given in Figure 1. A vehicular compartment heater (multifuel burning, NSN-2540-01-169-5159, S/N 11882, manufactured by Stewart-

Schematic of Vehicular Compartment Heater

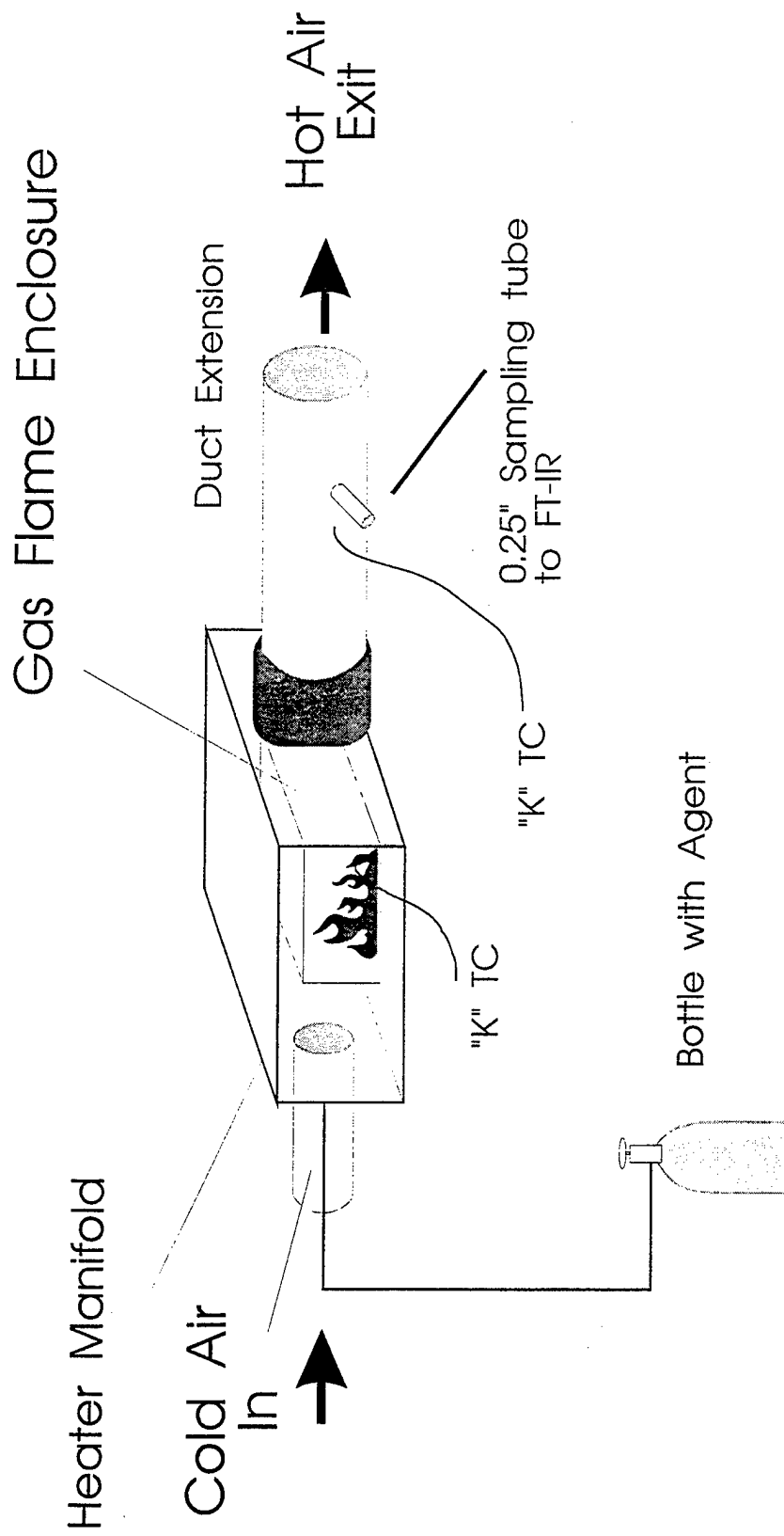


Figure 1. Schematic diagram of the experimental setup used to collect the FT-IR absorption spectra. Air is heated by flowing over the gas flame enclosure.

test stand (see Figure 1). The test was performed outdoors. Infrared spectra of gases removed from the hot air output duct of the personnel heater were measured using a Midac Corporation Model G-5001-FH Fourier transform spectrometer system operating at 0.5-cm^{-1} resolution. Detection of the infrared radiation was by a liquid nitrogen-cooled Hg-Cd-Te detector. The interior of the spectrometer was purged with dry nitrogen. The spectrometer was ruggedized for outdoor use by the manufacturer. The gas samples were removed from the hot air output duct via a 0.25-in-diameter stainless steel tube in series with a 10-m path-length multipass optical cell and a mechanical vacuum pump. The distance between the hot air output duct and the spectrometer was 5 m. The gas samples were continuously flowed through a 10-m path-length multipass optical gas cell (internal volume approximately $2,300\text{ cm}^3$) contained within the FT-IR spectrometer. The multipass cell was maintained at a constant temperature of 125° C .

A "K" type thermocouple (chromel-alomel) was mounted on the body of the personnel heater heat exchanger. Another "K" type thermocouple was installed in the exhaust duct approximately 42 in from the exit. A third "K" type thermocouple was installed to measure the ambient air temperature. The airflow through the system was measured using a Kurtz Model 441-S Air Velocity Meter inserted into the duct parallel to the airflow. The airflow was measured with the heater air induction blower on and the heater element turned off. The temperature-corrected airflow for this test was calculated to be 660 cfm at 495° C .

The personnel heater was ignited and allowed to operate until the heat exchanger surface and hot air output temperatures had stabilized. After the heater temperature had stabilized, but before the introduction of the agent into the heater air induction port, gas flow from the probe through the spectrometer optical system was begun by opening a valve between the vacuum pump and the exit port of the multipass optical cell. Upon establishment of gas flow from the heater hot air output duct through the sampling tube and the multipass optical cell, acquisition of spectra was begun, with each spectrum consisting of 10 co-added scans measured at 0.5 cm^{-1} resolution. The time required for collection of each 10-scan spectrum was approximately 15 s. Approximately 1 min after data acquisition was begun, chemical agent was allowed to flow through the heater air induction port, across the heat exchanger, and out the hot air output duct. Because of differences in viscosity and density, flow rate varied for each agent tested. Chemical agent flow was stopped after 4 liters of agents at a flow rate of 2 liters/min had been delivered. The FT-IR spectrometer continued to acquire spectra until no trace of agent could be observed in the spectra, after which the data acquisition was halted. Five fire-extinguishing agents (CF_3Br [tradename, Halon 1301],

All interferograms were transformed using triangular apodization, and the resulting single-beam infrared spectra ratioed to a spectrum measured prior to the chemical agent being introduced into the system.

3. RESULTS AND DISCUSSION

Figures 2–9 show infrared spectra (Rothman et al. 1992; National Institute of Standards and Technology 1992; Infrared Analysis, Inc. 1995) of the expected possible decomposition or combustion products for the fire-extinguishing agents tested. These products are HF, HBr, HCl, CF_3H , C_2H_2 , C_2H_4 , CH_4 , and CF_2O . Figures 10–12 are spectra of the agents Halon 1301 (CF_3Br), FM-200 ($\text{C}_3\text{F}_7\text{H}$), and FE-25 ($\text{C}_2\text{F}_5\text{H}$). Note that the possible decomposition product CF_3H shown in Figure 6 is the agent FE-13.

As an example of gases produced during chemical suppression of large-scale "real" fires, Figure 13 shows the infrared absorbance spectrum of a gaseous sample removed from a JP-8 fuel fire burning in air, after the application of a small amount of the fire inhibitor CF_3Br . Figure 14 presents the same data as Figure 13 but with spectral regions expanded for analysis. These spectra are shown for comparison with the present work. Evident in Figure 14 are the spectral features due to the hydrocarbon-fueled (JP-8) fire (i.e., H_2O , CO_2 , CO, CH_4 , C_2H_2 , and C_2H_4). Also present in this spectrum are the absorption features of the fire inhibitor CF_3Br , and the halon decomposition products HF, HBr, HCl, CF_3H , and CF_2O . The source of the HCl is believed to be chlorine impurities in the CF_3Br .

Figure 15 shows the infrared absorption spectrum of a gaseous sample removed from the personnel heater hot air output duct, during flow of Halon 1301 through the heater air induction port, while the heater manifold temperature was maintained at 380° C. Evident in this spectrum are intense absorptions of the fundamental bands for CF_3Br at 760, 1,080, and 1,200 cm^{-1} . These absorptions are saturated (i.e., there was sufficient agent concentration in the optical path to absorb all infrared radiation at frequencies corresponding to agent fundamental vibrations). Also evident in the spectrum are absorptions from CO_2 and H_2O . Within the limits of detection of the instrument, no evidence for the decomposition or combustion products of CF_3Br , HF, HBr, HCl, CF_3H , CO, CF_2O , C_2H_2 , or C_2H_4 was seen.

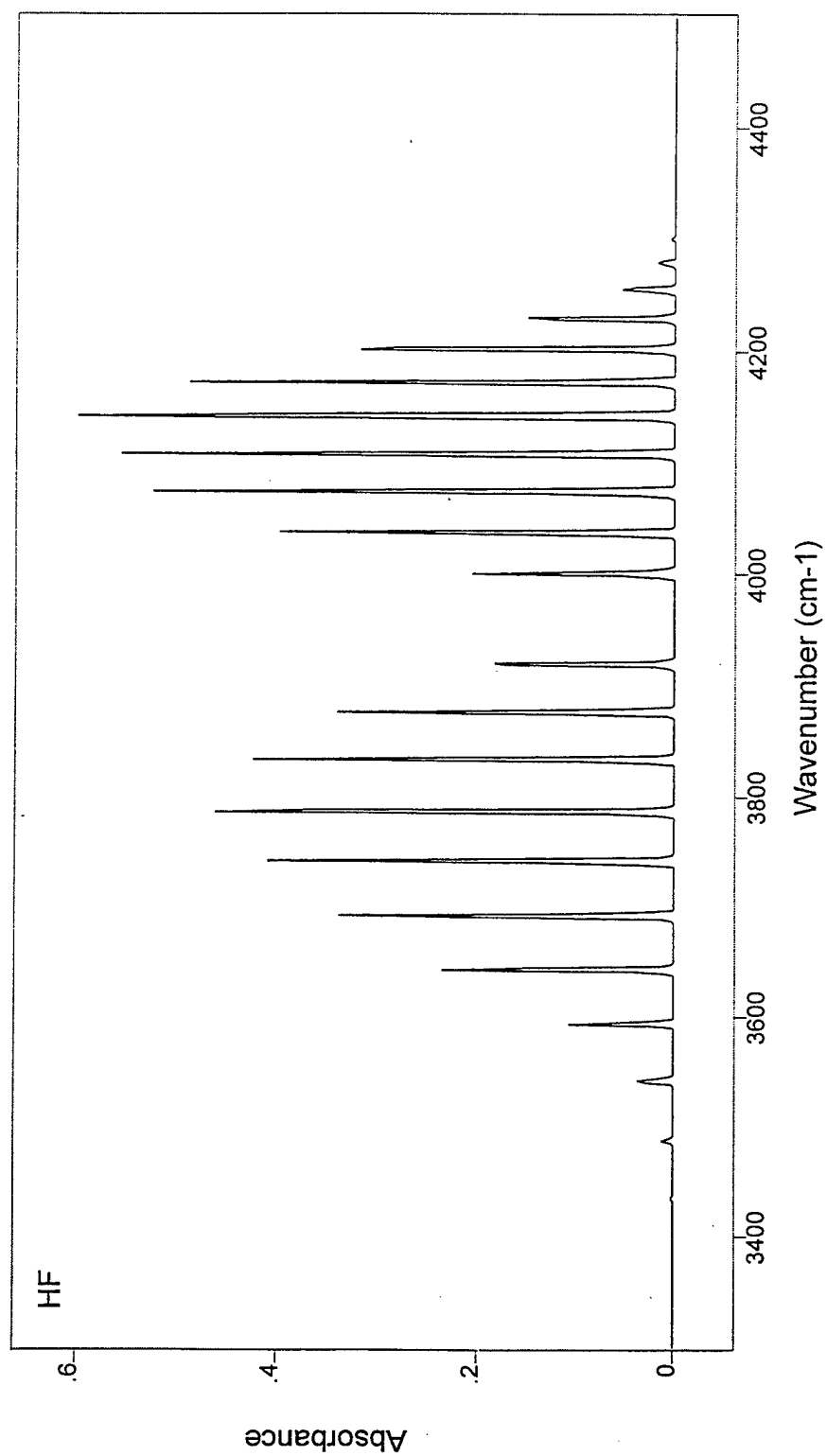


Figure 2. Reference spectrum of HF generated with the HITRAN database. The parameters used to produce the spectrum are as follows: conc. = 10 ppm, T = 125° C.

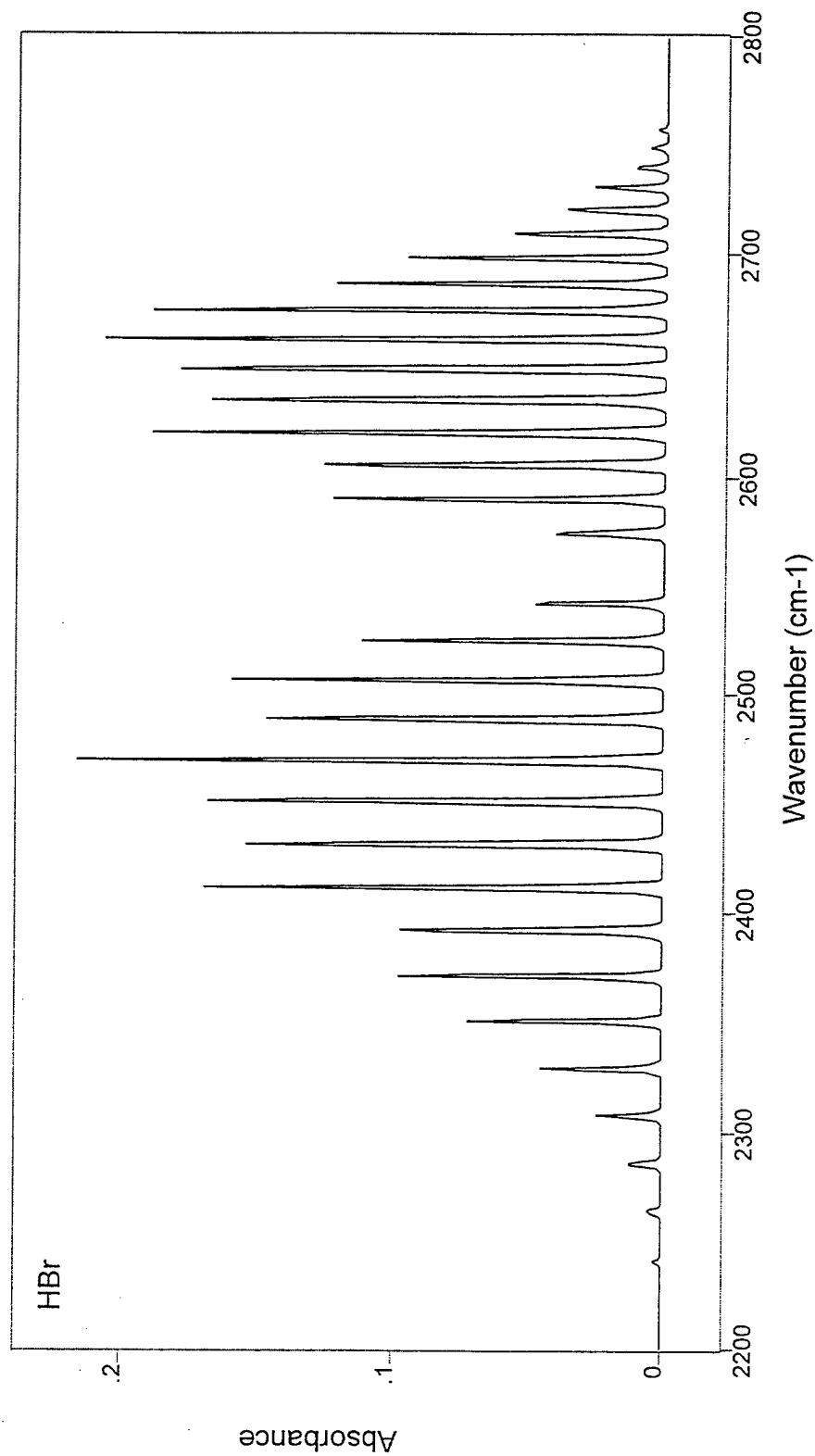


Figure 3. Reference spectrum of HBr generated with the HITRAN database. The parameters used to produce the spectrum are as follows: conc. = 100 ppm, T = 125° C.

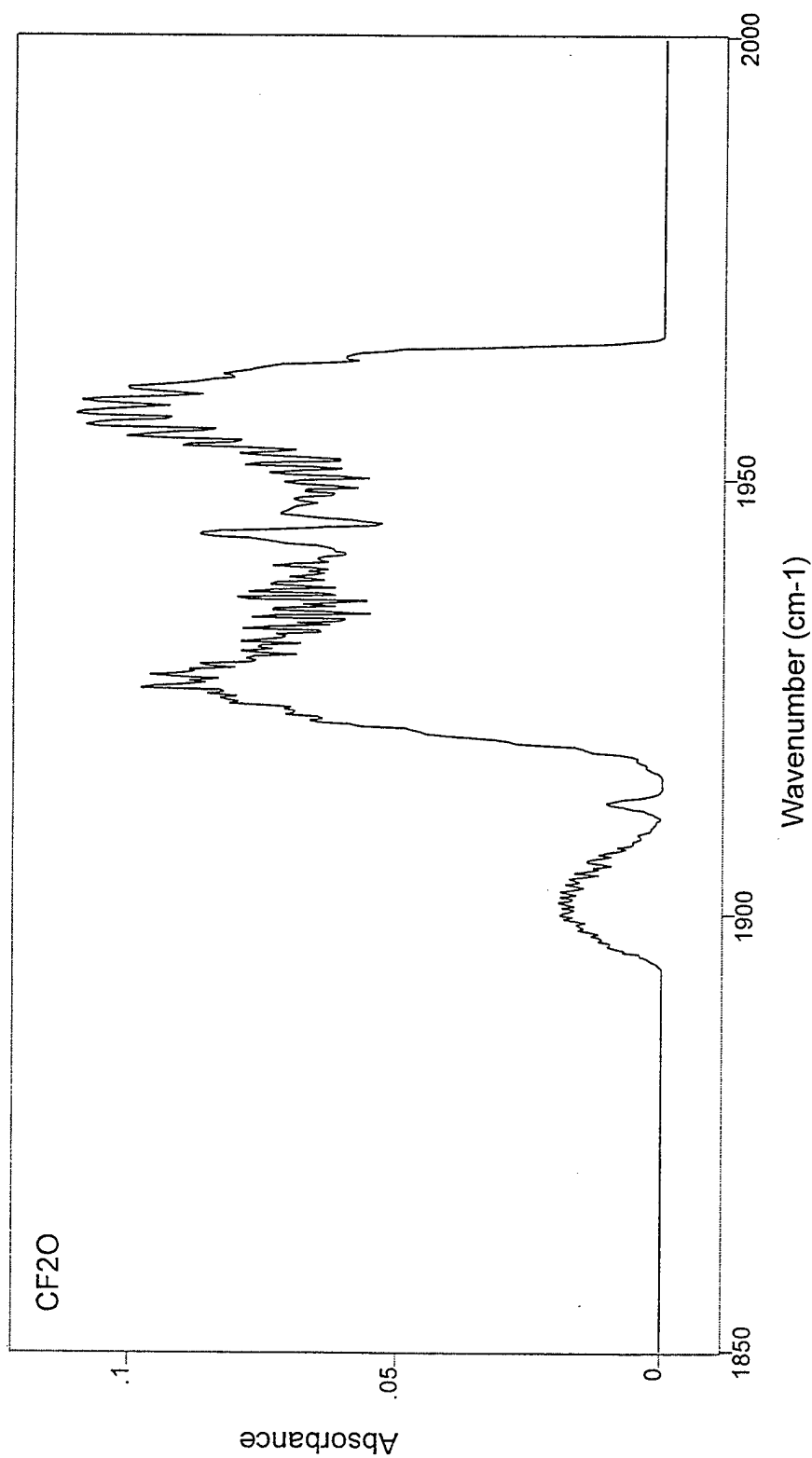


Figure 4. Reference spectrum of CF_2O generated with the HITRAN database. The parameters used to produce the spectrum are as follows:
conc. = 10 ppm, $T = 125^\circ\text{C}$.

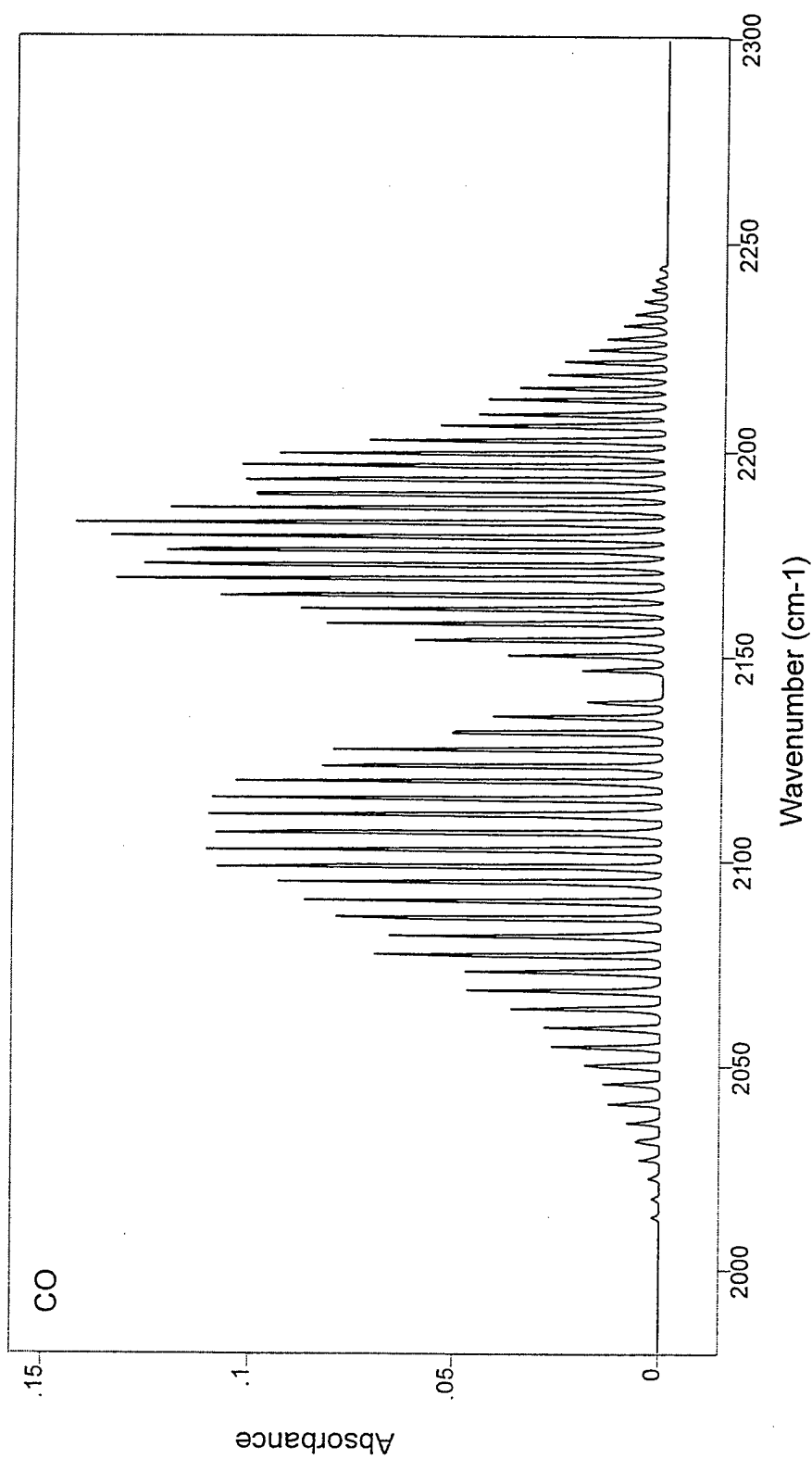


Figure 5. Reference spectrum of CO generated with the HITRAN database. The parameters used to produce the spectrum are as follows:
conc. = 10 ppm, T = 125° C.

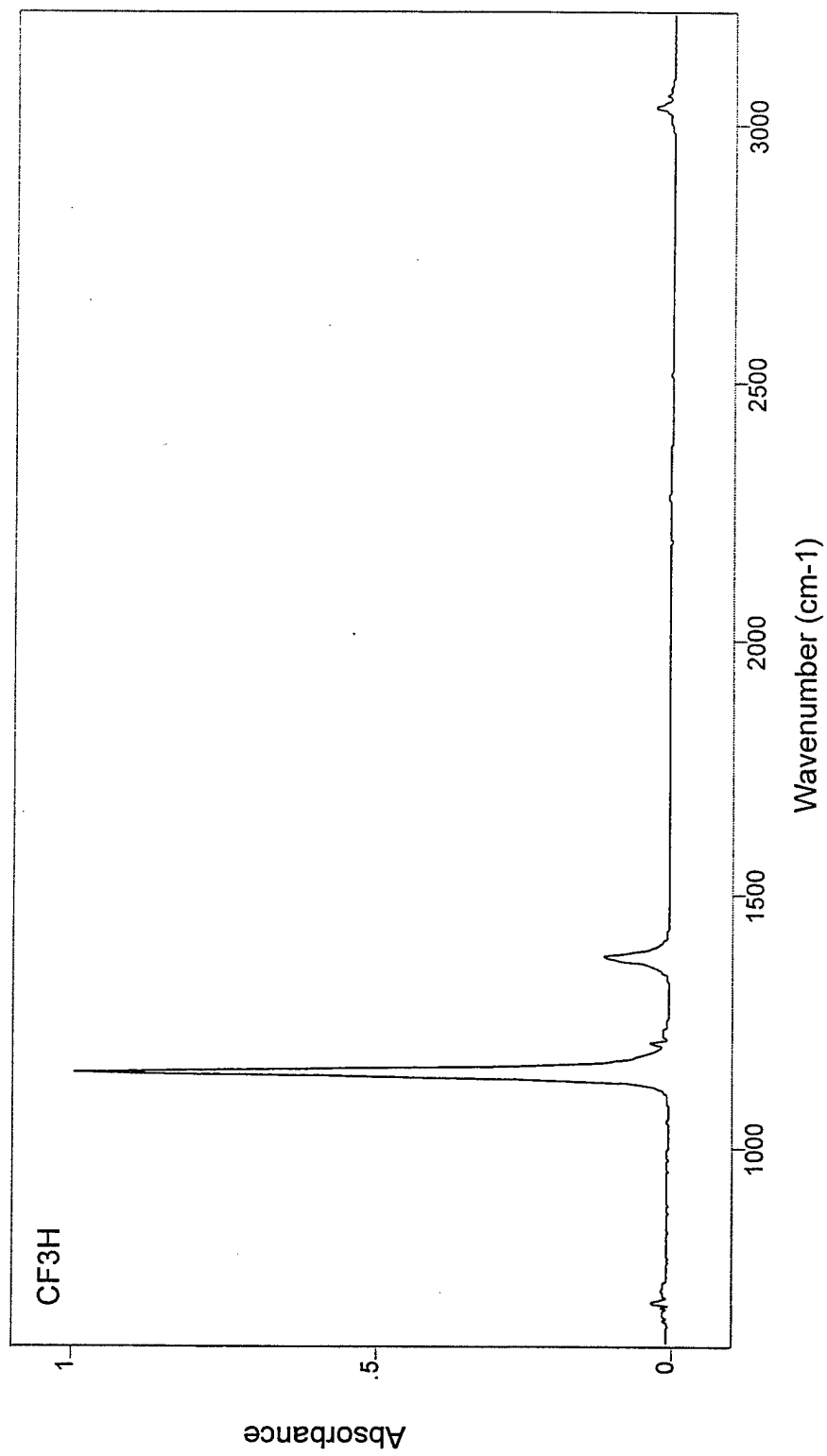


Figure 6. Reference spectrum of CF₃H (FE-13) generated with the EPA database. The parameters used to produce the spectrum are not available.

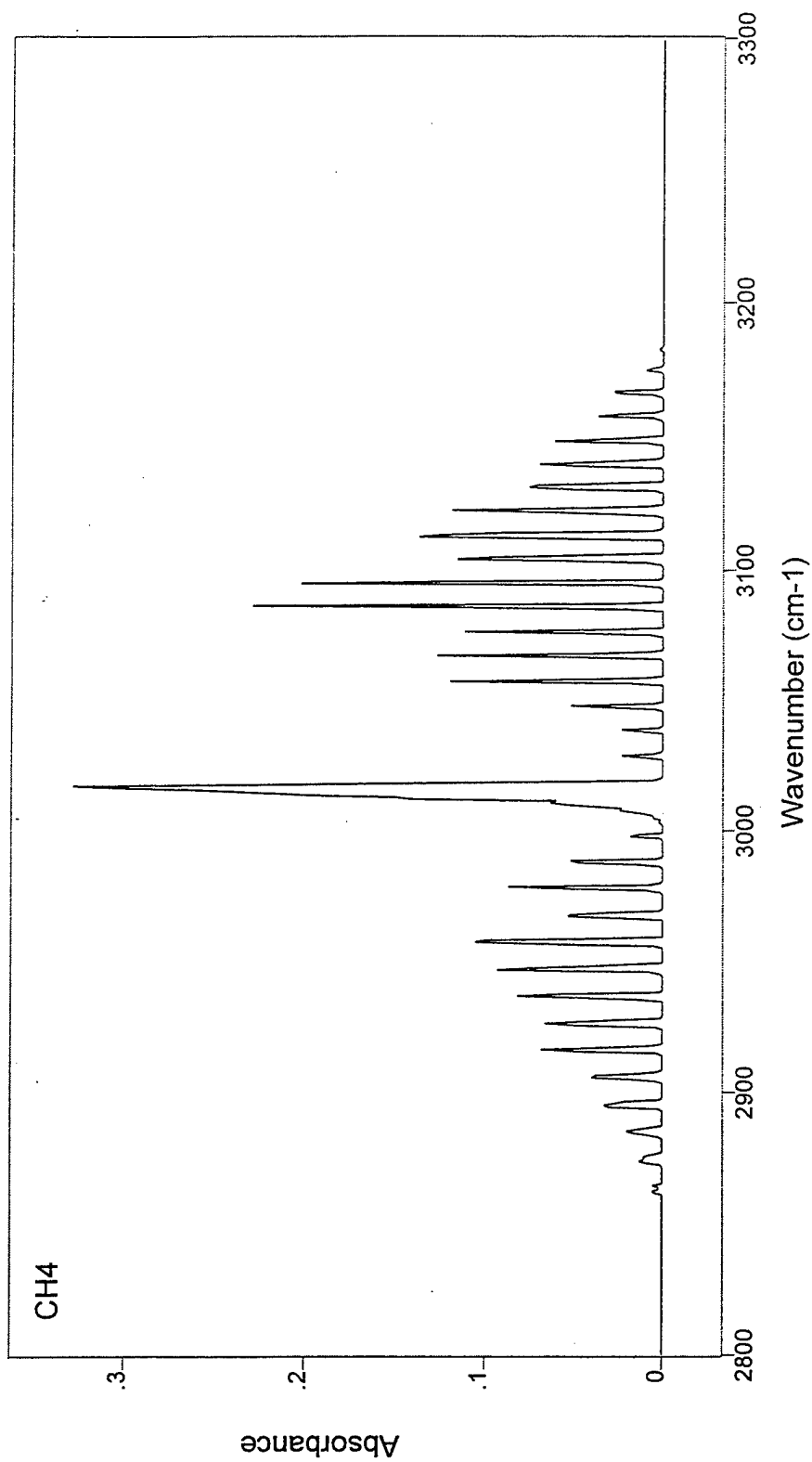


Figure 7. Reference spectrum of CH₄ generated with the HITRAN database. The parameters used to produce the spectrum are as follows:
conc. = 10 ppm, T = 125° C.

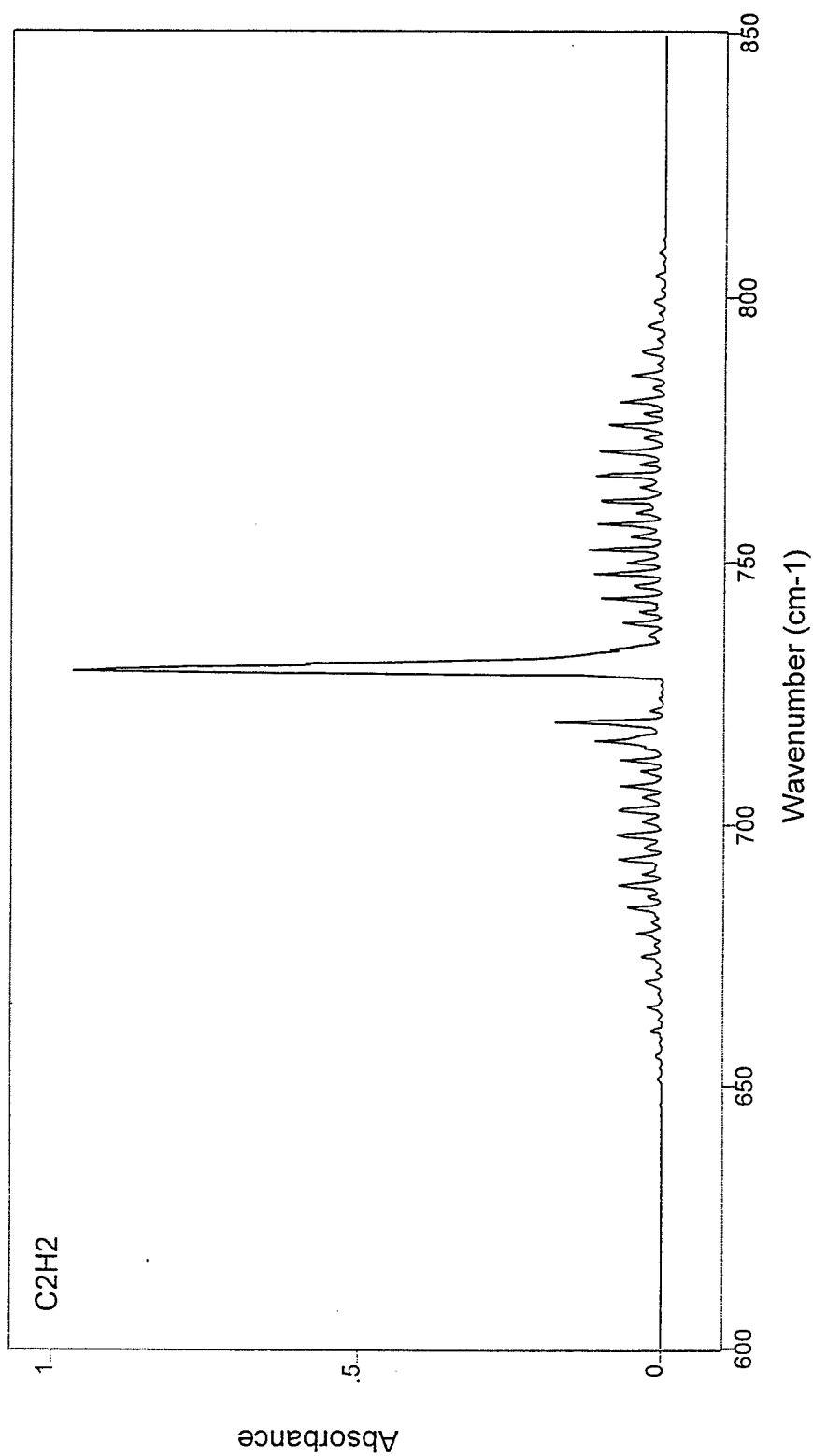


Figure 8. Reference spectrum of C_2H_2 generated with the HITRAN database. The parameters used to produce the spectrum are as follows:
conc. = 10 ppm, $T = 125^\circ C$.

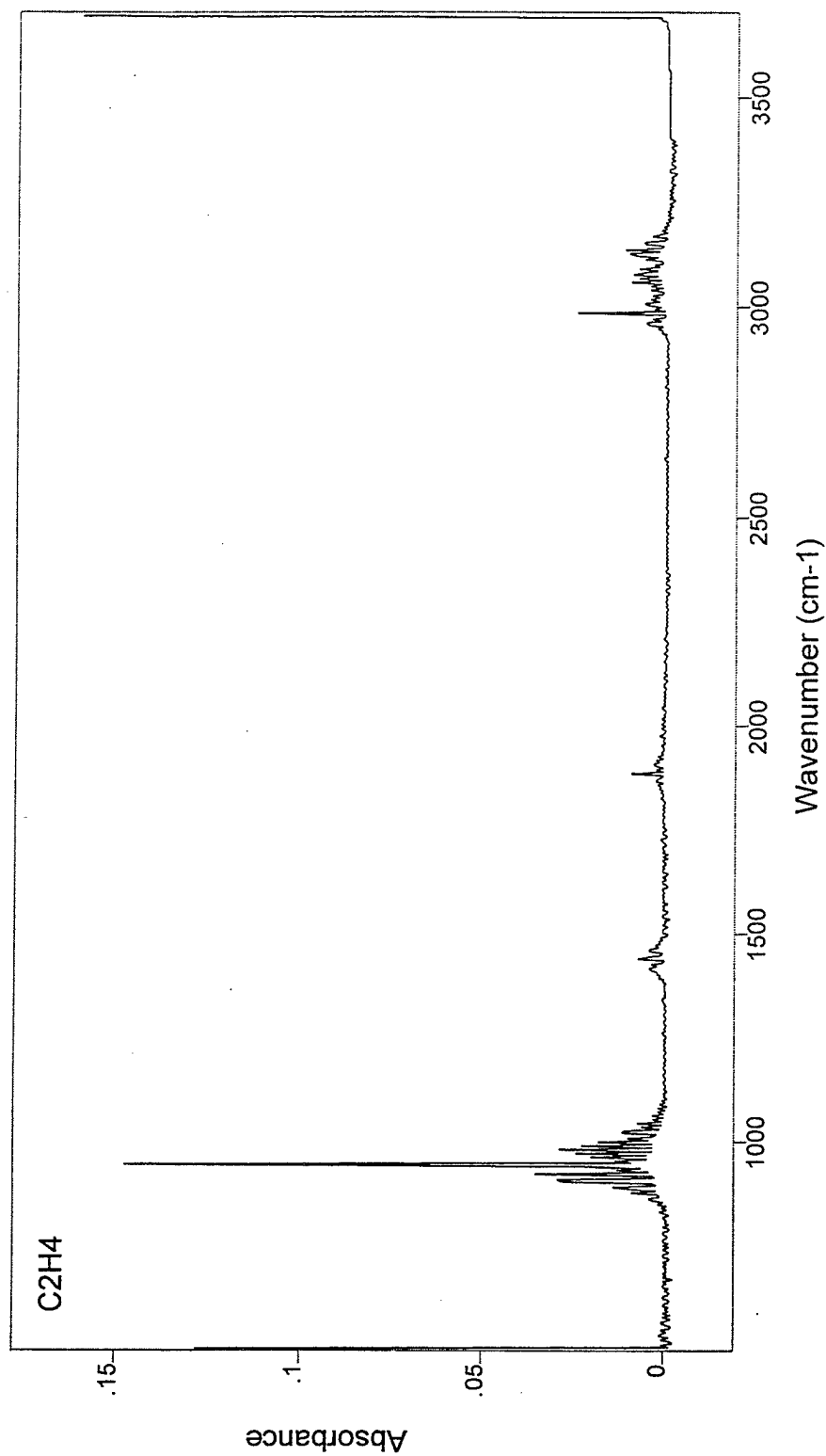


Figure 9. Reference spectrum of C_2H_4 generated with the QaSoft database. The parameters used to produce the spectrum are as follows: conc. = 100 ppm-m, $T = 25^\circ C$.

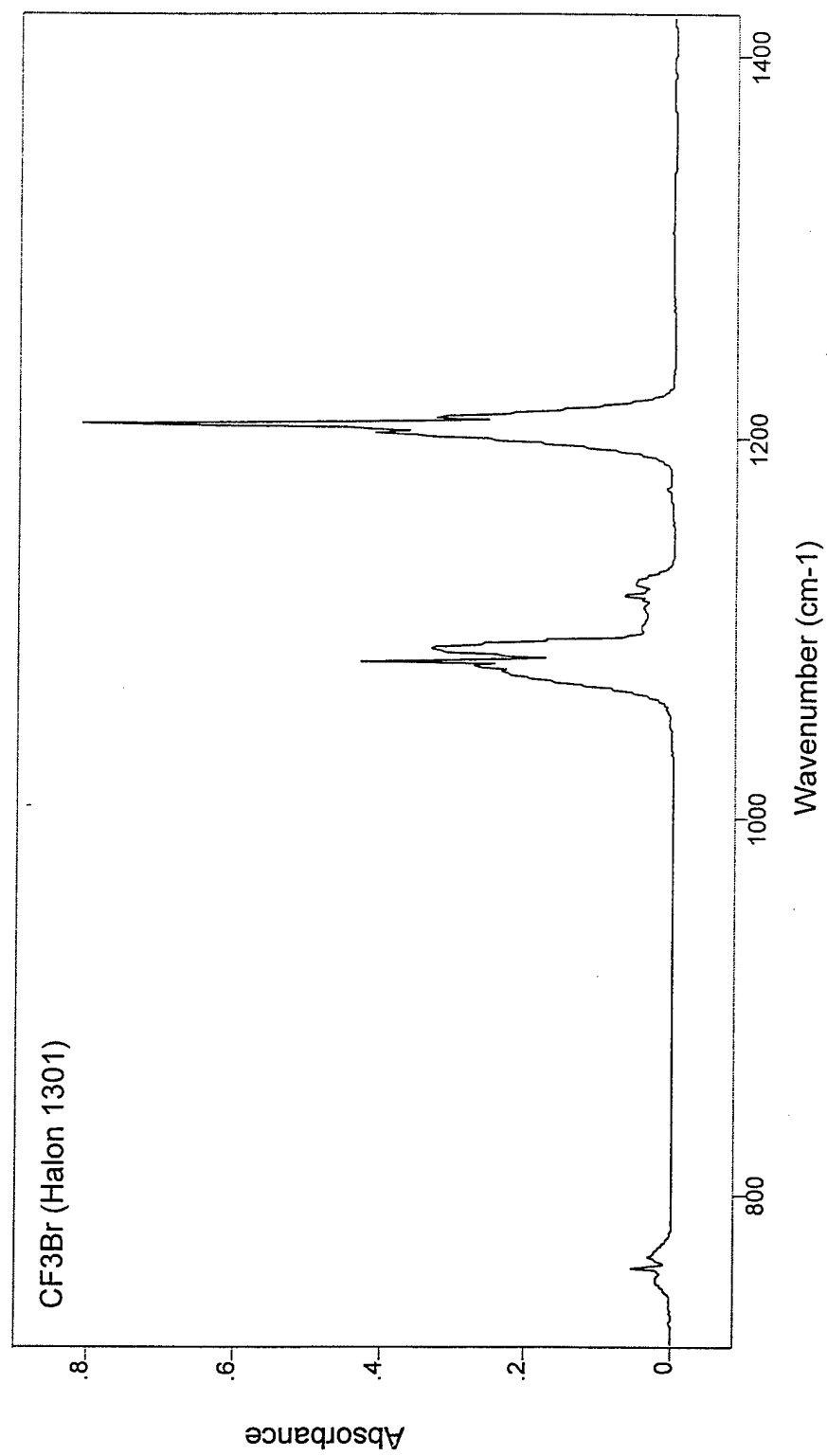


Figure 10. Reference spectrum of CF₃Br (Halon 1301) generated from the QaSoft database. The parameters are 100 ppm-m at 25° C.

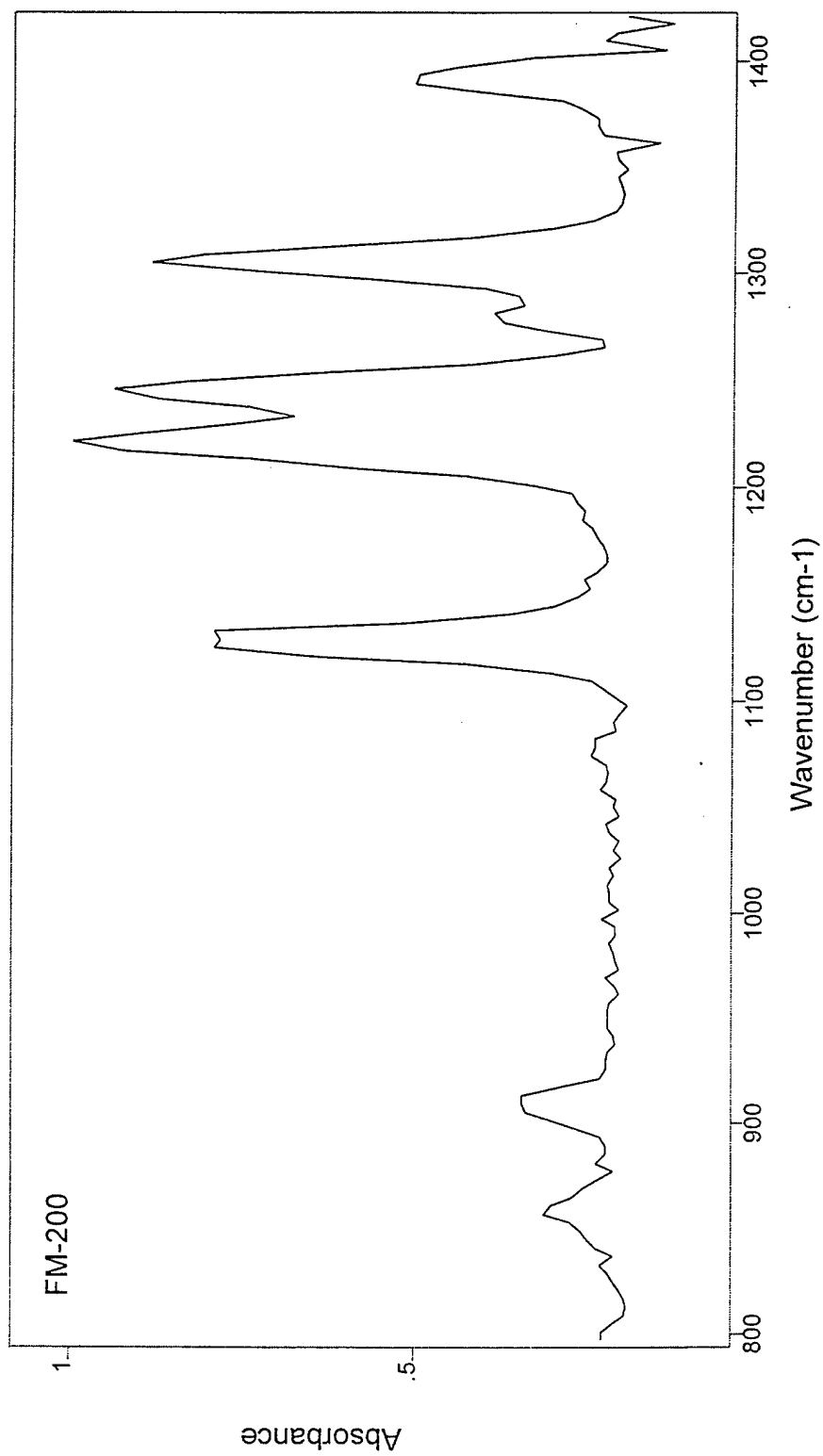


Figure 11. Reference spectrum of C₃F₇H (FM-200) measured in our laboratory.

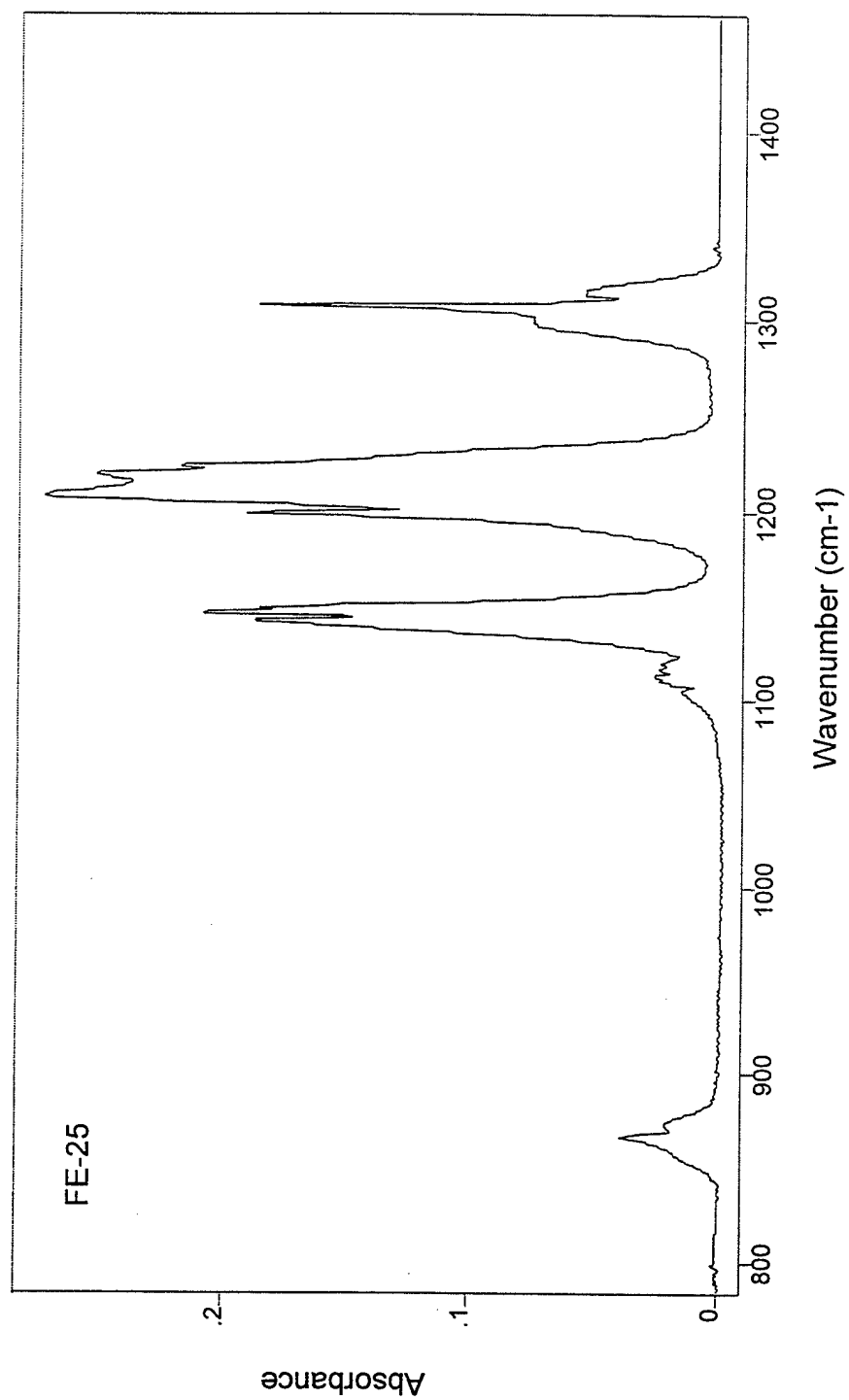


Figure 12. Reference spectrum of C_2F_5H (FE-25) from the QaSoft database. The parameters used to produce the spectrum are as follows: conc. = 100 ppm-m, $T = 25^\circ C$.

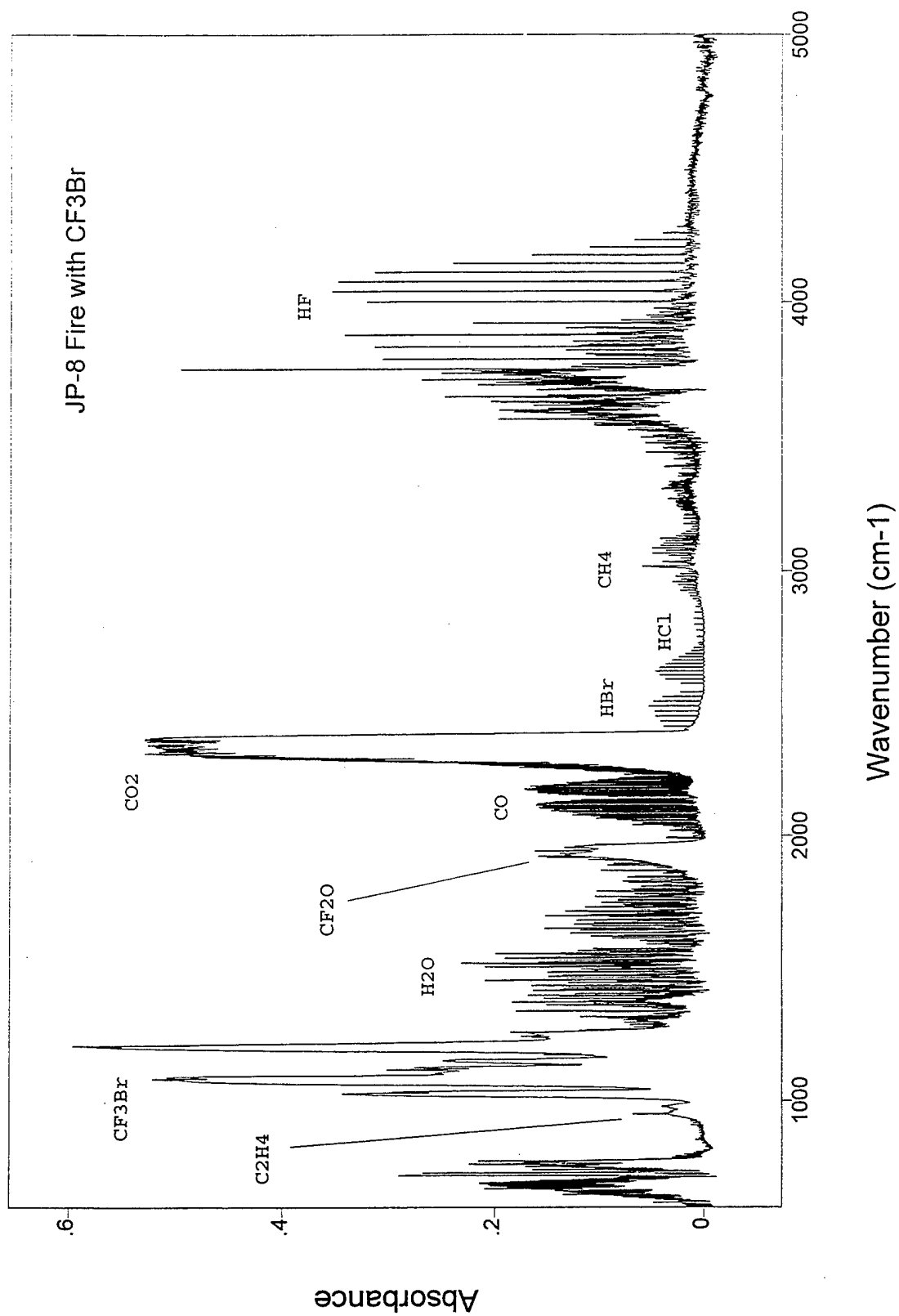


Figure 13. The infrared absorbance spectrum of gas removed from the vicinity of a JP-8 fuel pool fire 15 s after the application of approximately 0.5 kg of CF₃Br.

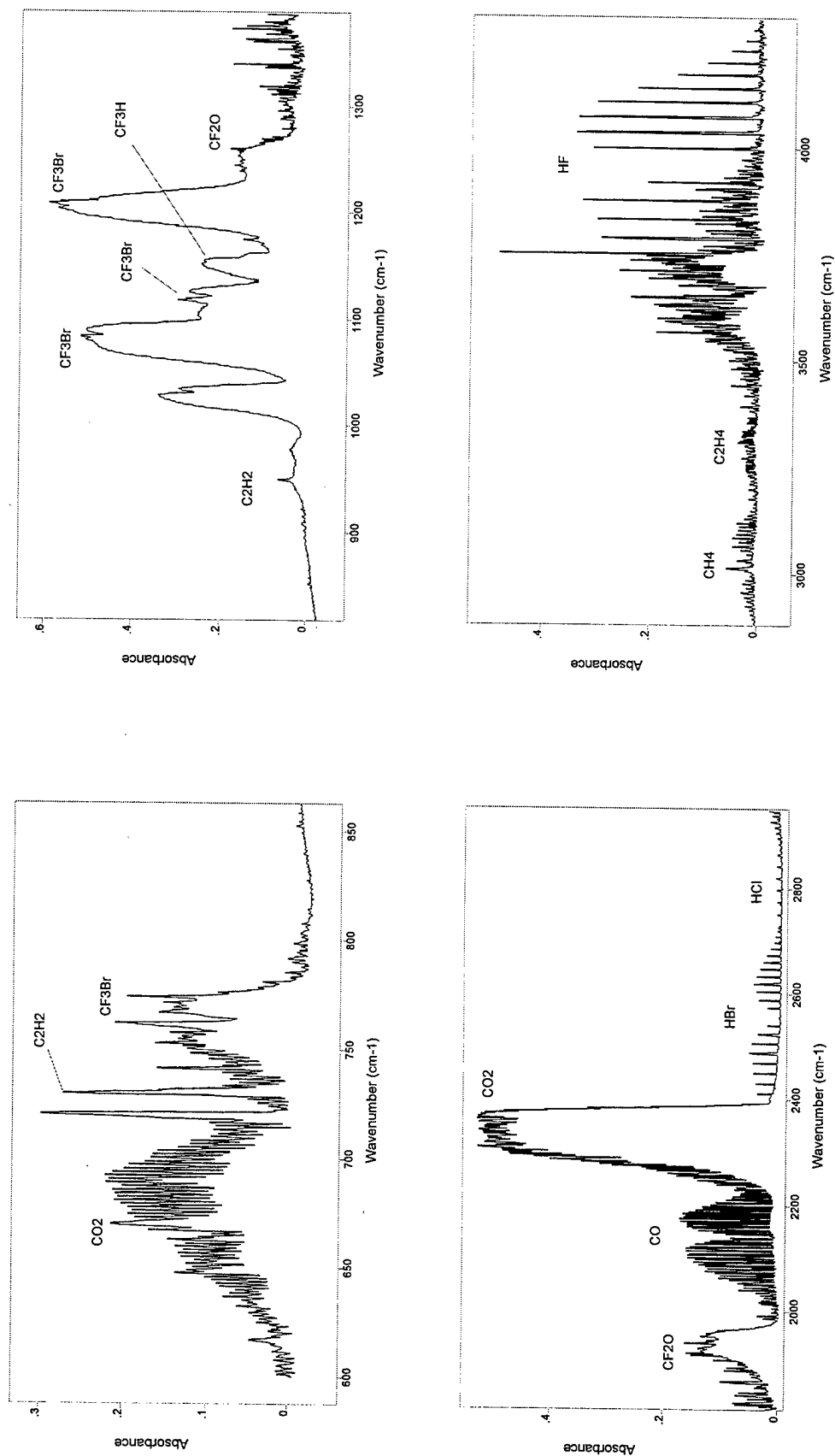


Figure 14. Expanded regions of the infrared absorbance spectrum of gas removed from the vicinity of a JP-8 fuel pool fire 15 s after the application of approximately 0.5-kg CF_3Br (Halon 1301).

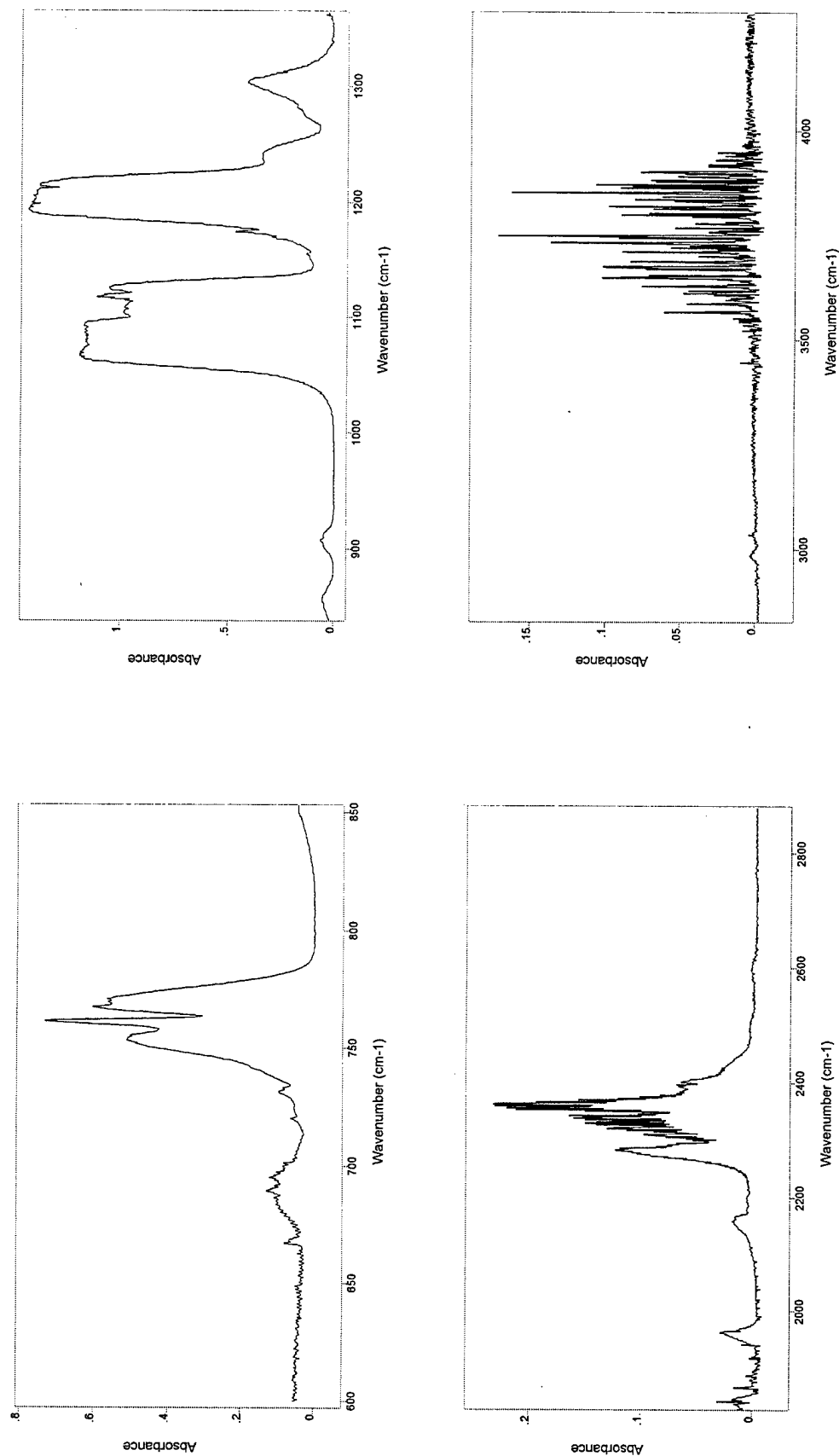


Figure 15. Expanded regions of the infrared absorbance spectrum of a gas sample removed from the personnel heater exit port while the fire-extinguishing agent Halon 1301 is flowed across the heat exchanger manifold. The heat exchanger manifold temperature was maintained at 380° C.

Figure 16 shows the infrared absorption spectrum of a gaseous sample removed from the personnel heater hot air output duct, during flow of Halon 1301 through the heater air induction port, while the heater manifold temperature was maintained at 510° C. This spectrum is similar to that measured for the analogous experiment at 380° C. Again, within the limits of detection for the instrument, no evidence of the decomposition products of Halon 1301 was seen.

Figures 17–24 present similar results for FM-200, FE-36, FE-25, and FE-13 for both temperature ranges used in these tests. Again, within the limits of detection for the instrument, no evidence of agent decomposition or combustion products (CF_3Br , HF , HBr , HCl , CF_3H , CO , CF_2O , C_2H_2 , or C_2H_4) was seen.

A closer examination of the spectra of FM-200, FE-36, FE-25, and FE-13 revealed an unexpected consequence of the methodology used in the study. With the exception of Halon 1301 (the first gas to be studied), all subsequent agents were contaminated with the previous agent that was in the system. The order in which the agents were studied for both temperature conditions was as follows: Halon 1301, FM-200, FE-36, FE-25, FE-13, and then Halon 1301 was repeated. This sequence was done for the lower temperature and then repeated for the higher temperature. This contamination problem was caused by improperly evacuating the gas cylinder used to hold the fire-extinguishing agent before it was refilled with the next agent to be tested.

Table 1 presents the minimum detection limits for each of the decomposition products of interest under the experimental conditions employed for these tests. The detection limit was defined as a spectral feature with a peak intensity three times larger than the peak-to-peak noise (in transmission). The detection limit was calculated using this peak intensity value and spectral parameters from the HITRAN92 Database (Rothman et al. 1992), for the species under consideration.

4. CONCLUSIONS

Five fire-extinguishing agents, CF_3Br , $\text{C}_3\text{F}_7\text{H}$, $\text{C}_3\text{F}_6\text{H}_2$, $\text{C}_2\text{F}_5\text{H}$, and CF_3H , were tested for possible decomposition after being discharged into the air induction port of a fuel-fired vehicle personnel heater. Gas samples removed from the personnel heater hot air output duct, while fire-extinguishing agents were flowed across the heat exchanger manifold, were examined using FT-IR spectroscopy. Within the limits of detection for the instrument, no evidence of agent decomposition or combustion products (HF , HBr , HCl , CF_3H , CO , CF_2O , C_2H_2 , or C_2H_4) was measured in these systems under the conditions of the test.

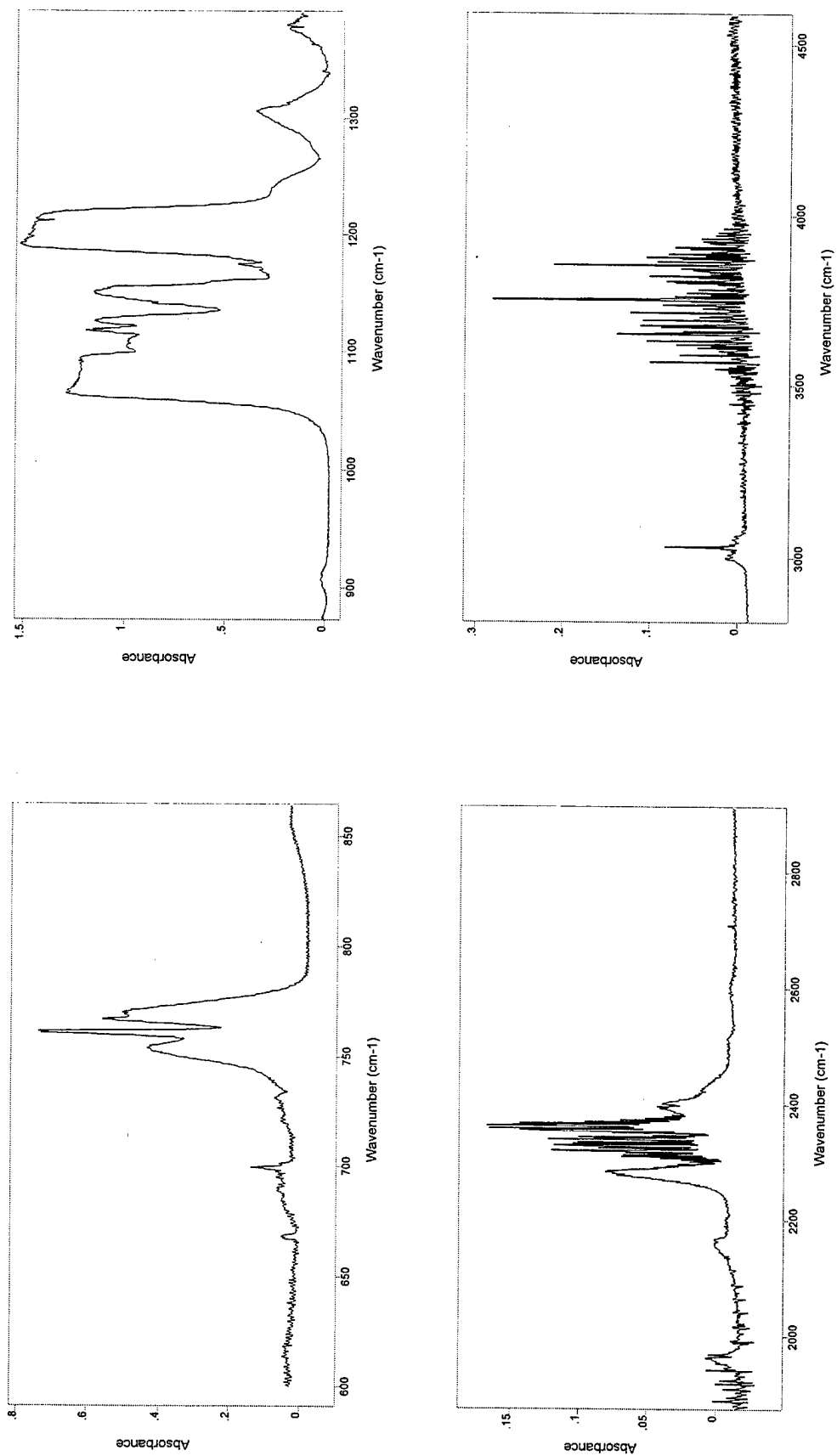


Figure 16. Expanded regions of the absorbance spectrum of a gas sample removed from the personnel heater exit port while the fire-extinguishing agent Halon 1301 is flowed across the heat exchanger manifold. The heat exchanger manifold temperature was maintained at 480-510° C.

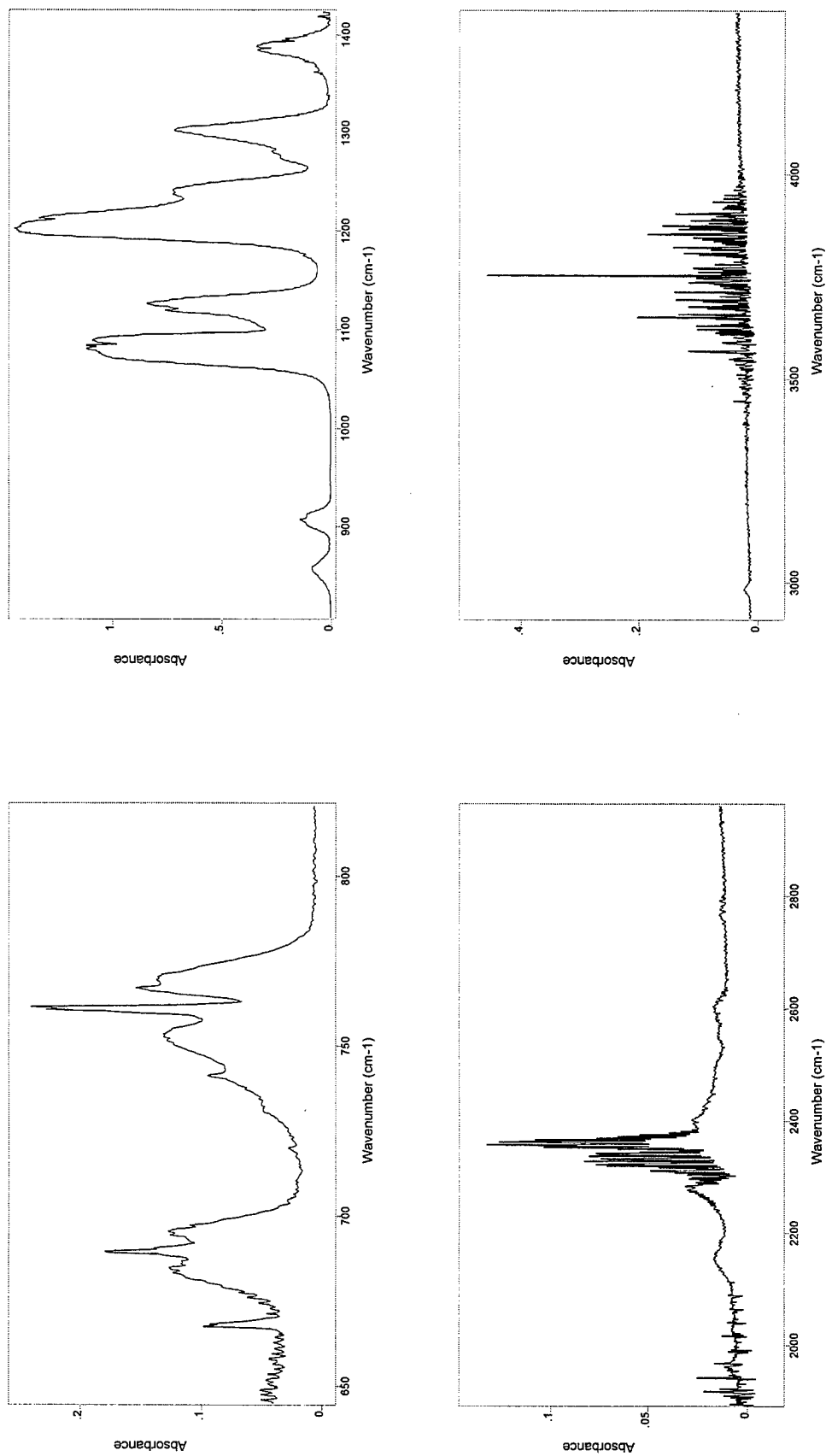


Figure 17. Expanded regions of the infrared absorbance spectrum of a gas sample removed from the personnel heater exit port while the fire-extinguishing agent FM-200 is flowed across the heat exchanger manifold. The heat exchanger manifold temperature was maintained at 380° C.

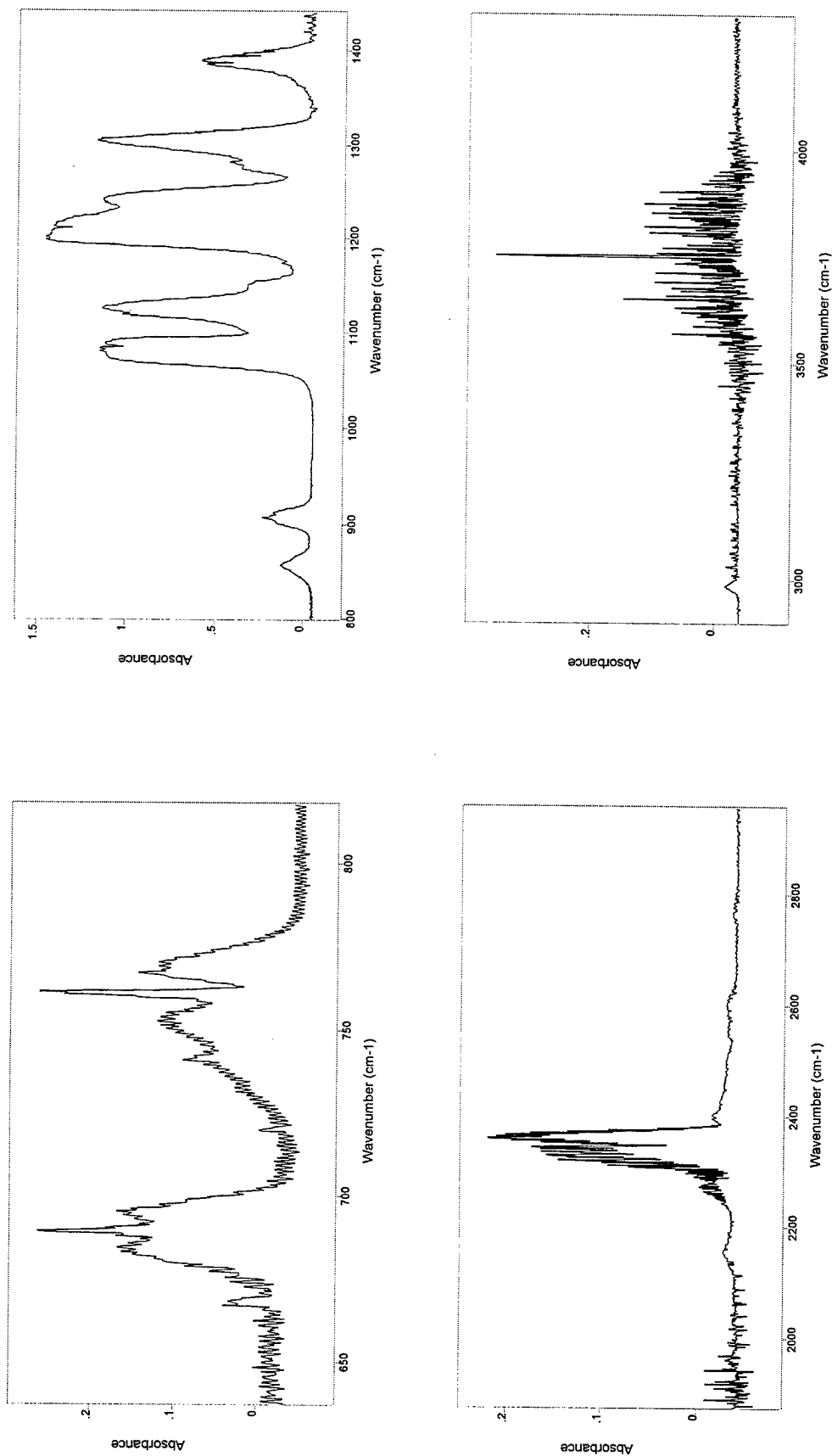


Figure 18. Expanded regions of the infrared absorbance spectrum of a gas sample removed from the personnel heater exit port while the fire-extinguishing agent FM-200 is flowed across the heat exchanger manifold. The heat exchanger manifold temperature was maintained at 480–510° C.

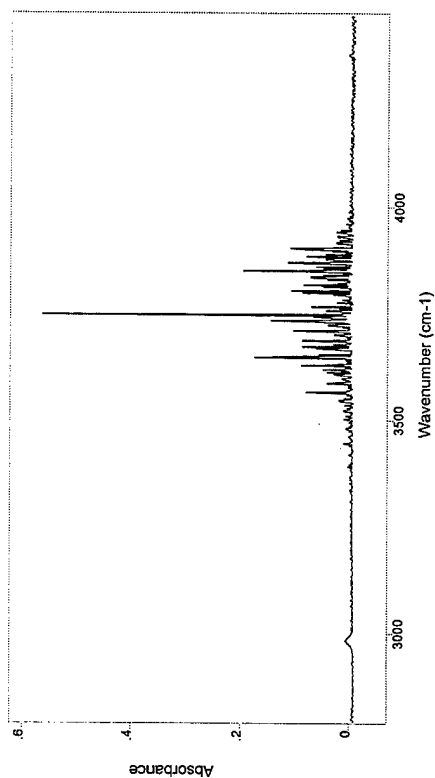
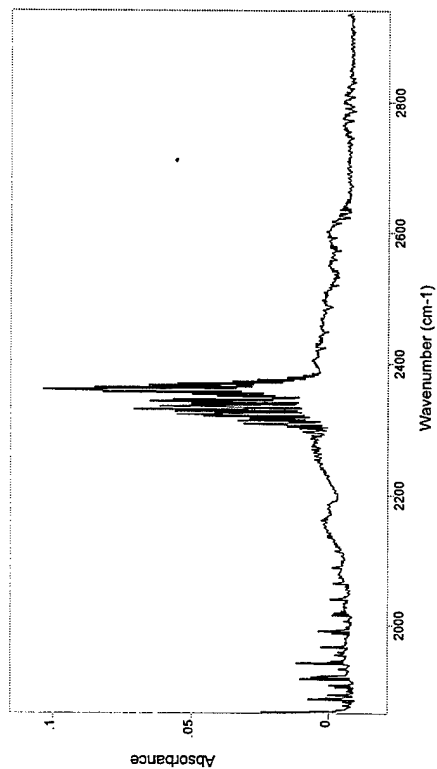
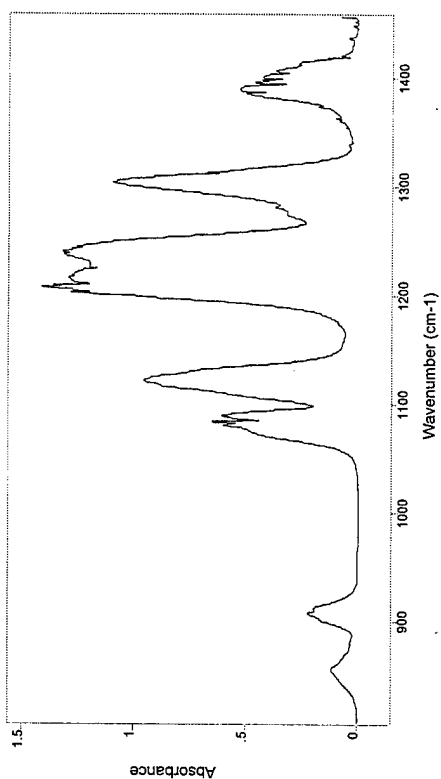
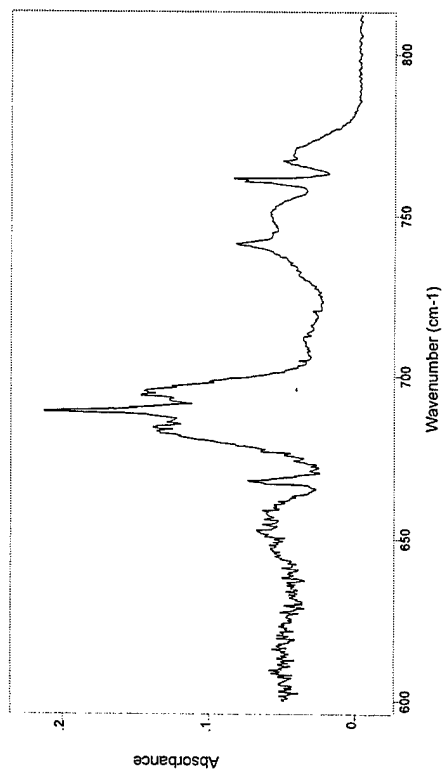


Figure 19. Expanded regions of the infrared absorbance spectrum of a gas sample removed from the personnel heater exit port while the fire-extinguishing agent FE-36 is flowed across the heat exchanger manifold. The heat exchanger manifold temperature was maintained at 380° C.

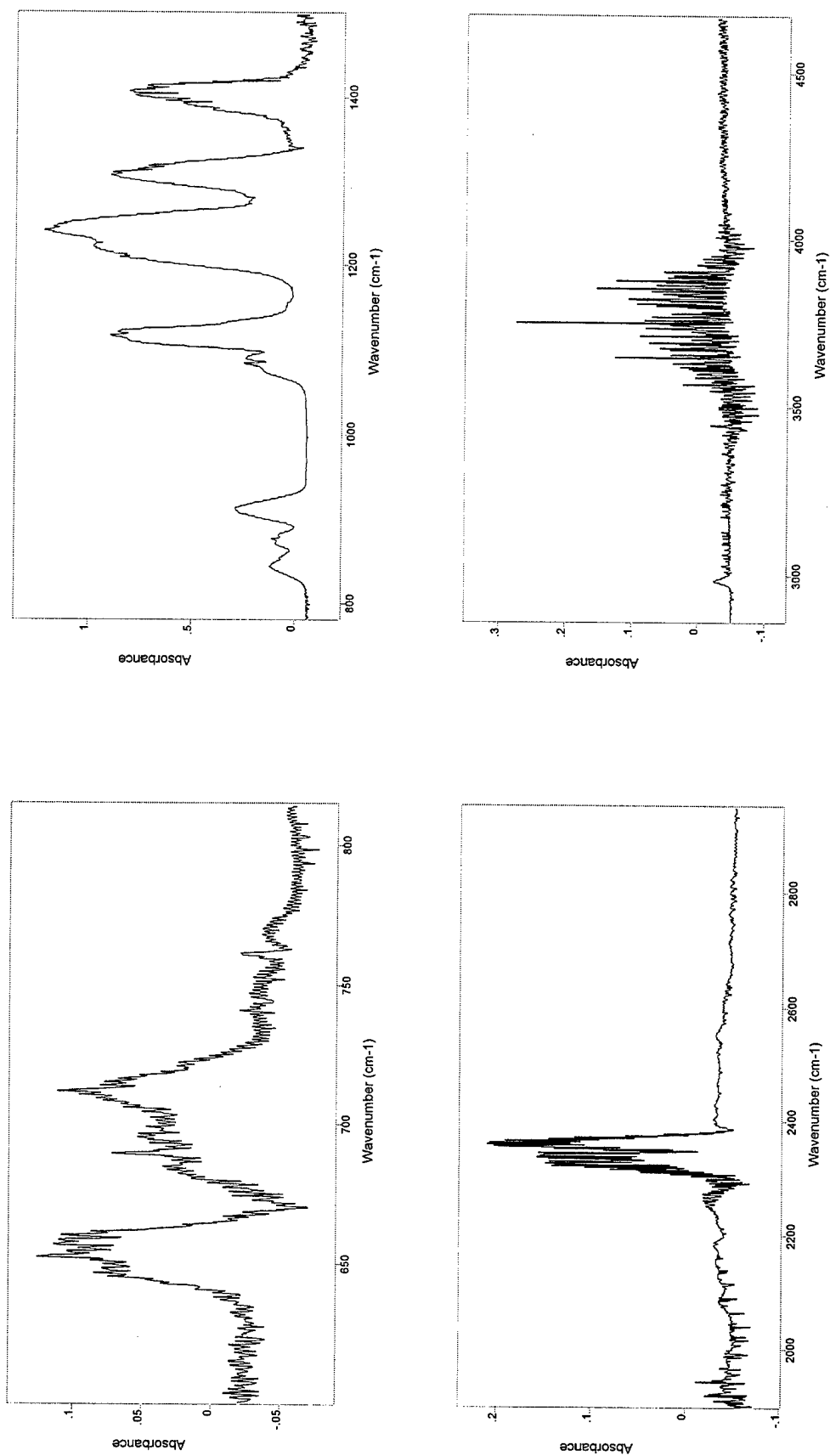


Figure 20. Expanded regions of the infrared absorbance spectrum of a gas sample removed from the personnel heater exit port while the fire-extinguishing agent FE-36 is flowed across the heat exchanger manifold. The heat exchanger manifold temperature was maintained at 480-510° C.

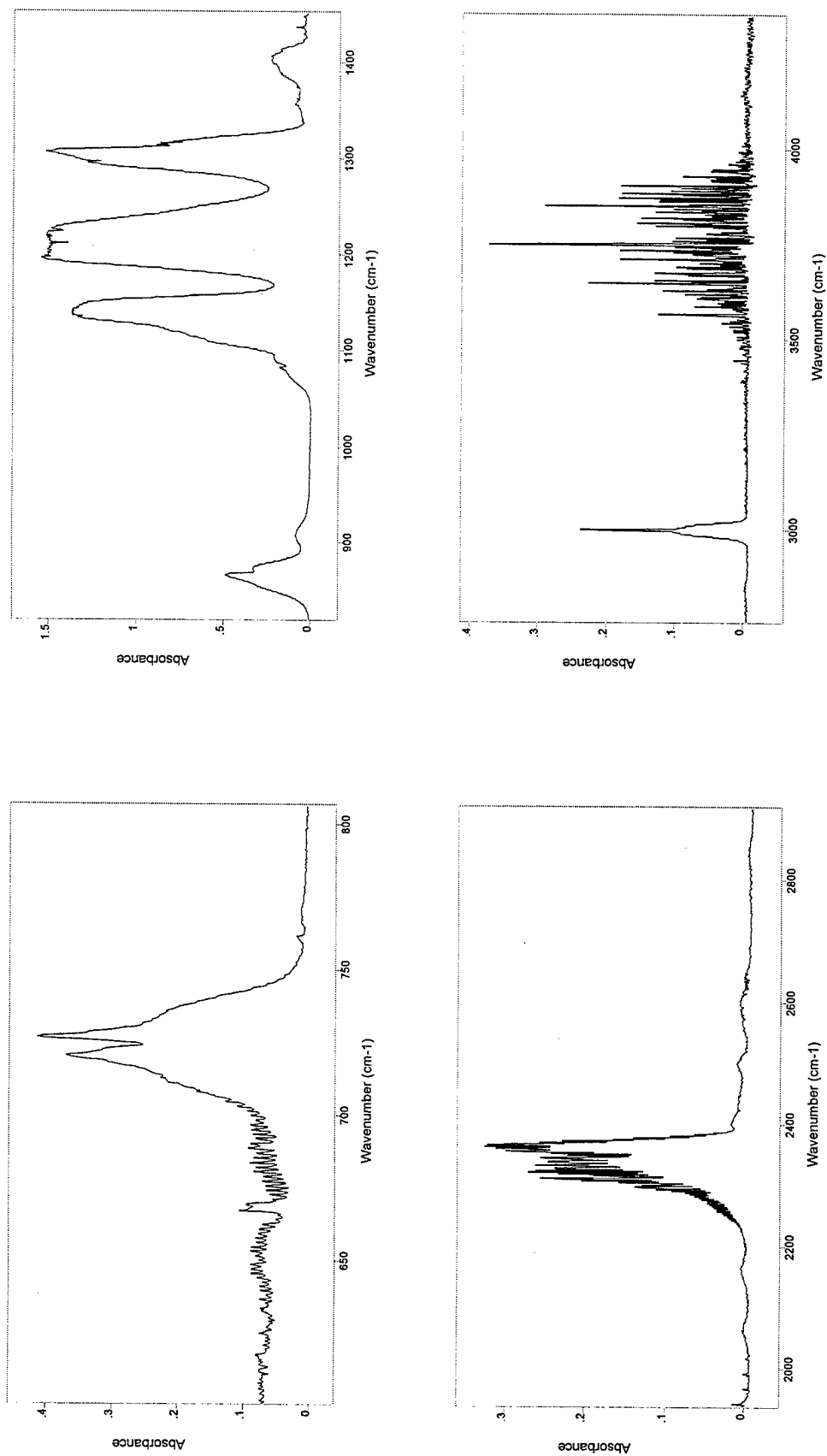


Figure 21. Expanded regions of the infrared absorbance spectrum of a gas sample removed from the personnel heater exit port while the fire-extinguishing agent FE-25 is flowed across the heat exchanger manifold. The heat exchanger manifold temperature was maintained at 380° C.

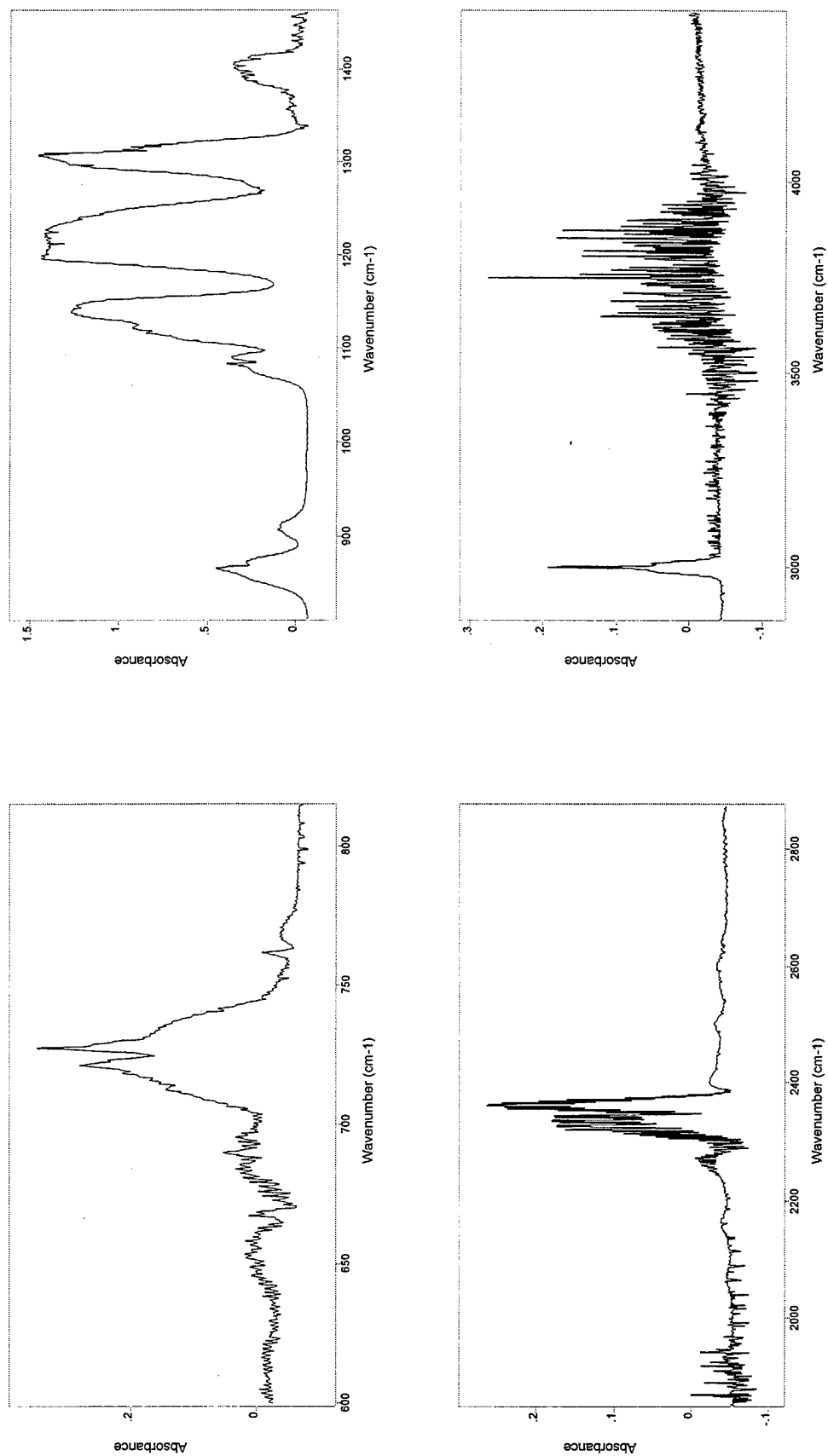


Figure 22. Expanded regions of the infrared absorbance spectrum of a gas sample removed from the personnel heater exit port while the fire-extinguishing agent FE-25 is flowed across the heat exchanger manifold. The heat exchanger manifold temperature was maintained at 480–510° C.

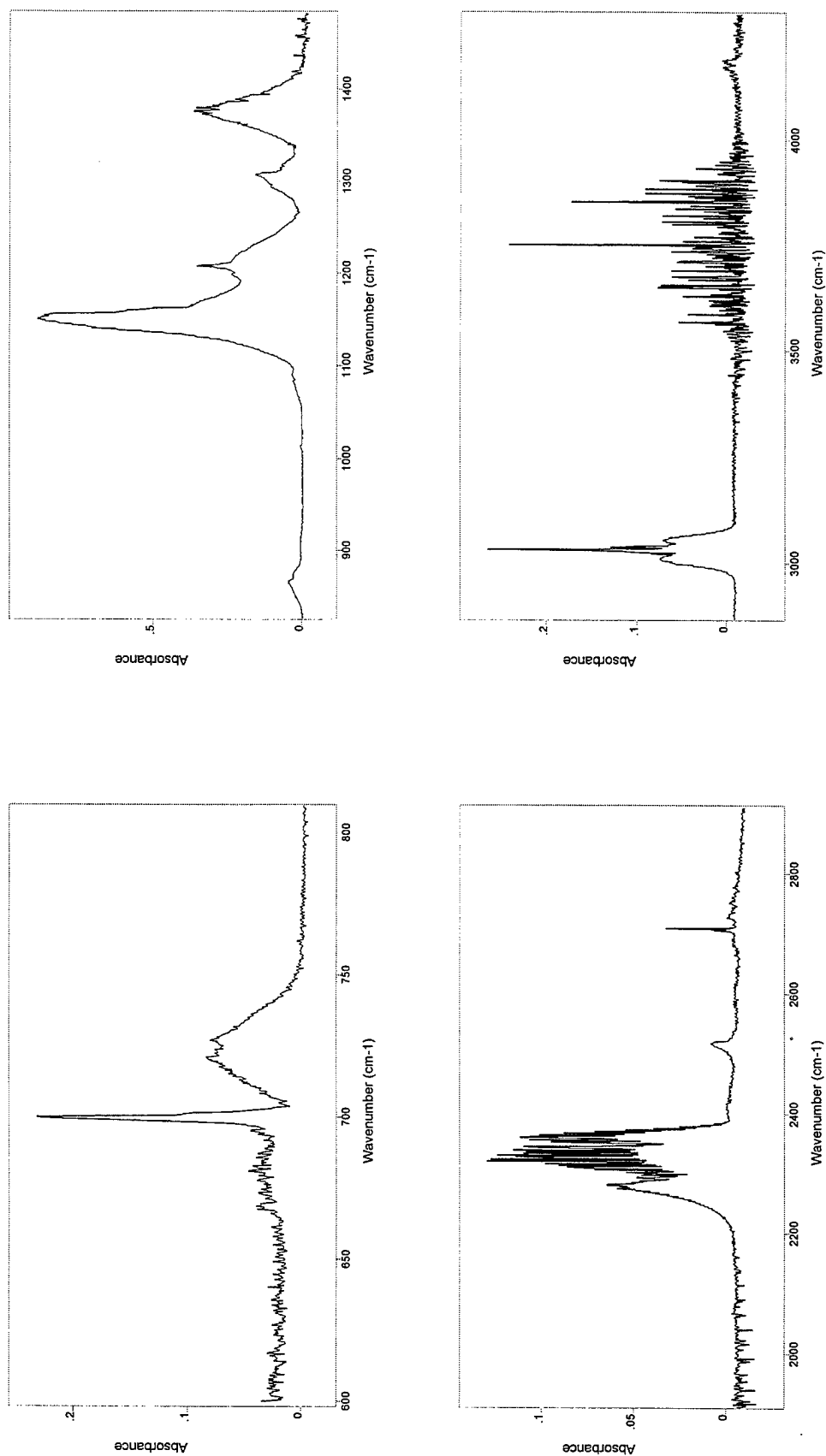


Figure 23. Expanded regions of the infrared absorbance spectrum of a gas sample removed from the personnel heater exit port while the fire-extinguishing agent FE-13 is flowed across the heat exchanger manifold. The heat exchanger manifold temperature was maintained at 380° C.

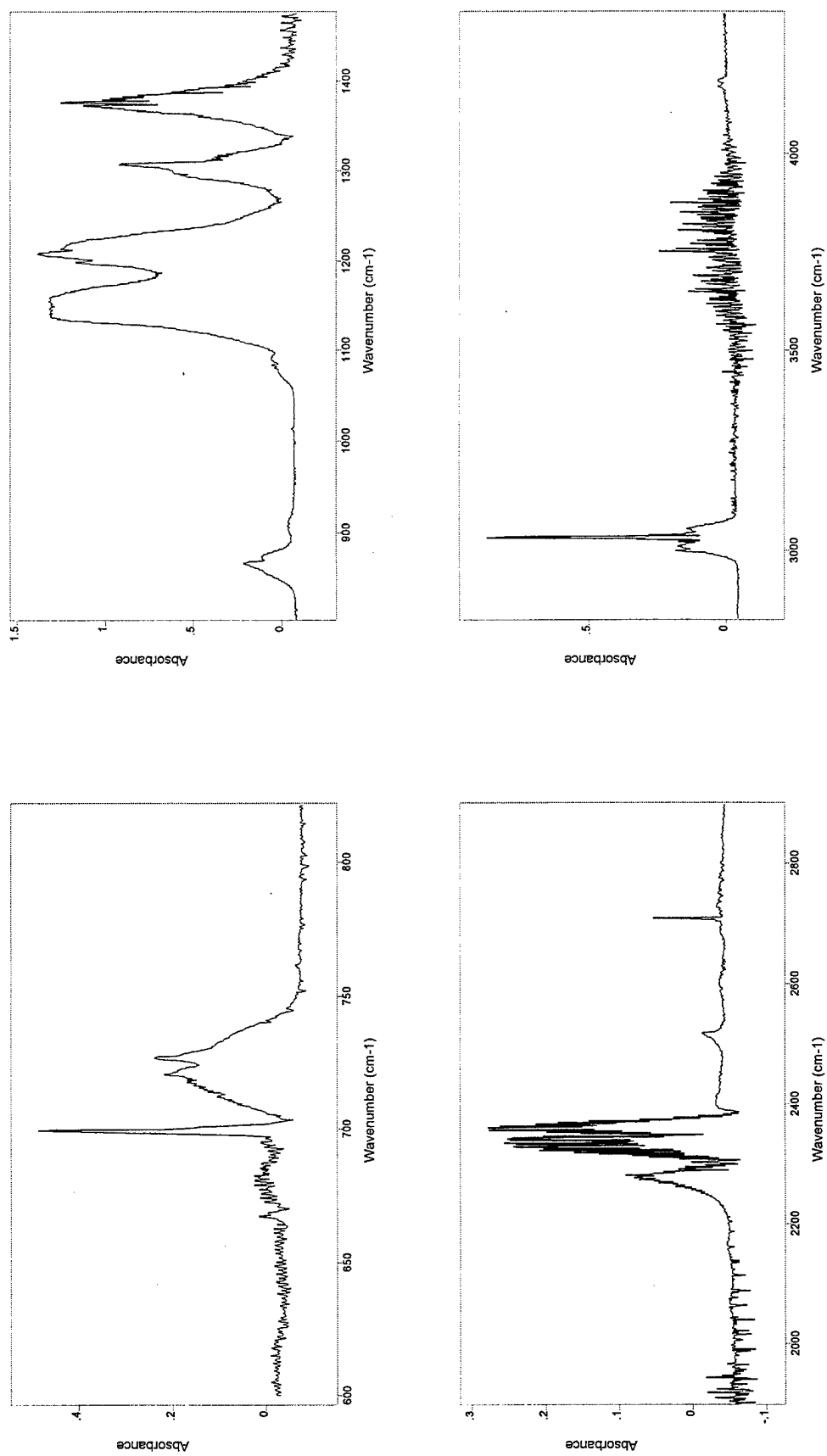


Figure 24. Expanded regions of the infrared absorbance spectrum of a gas sample removed from the personnel heater exit port while the fire-extinguishing agent FE-13 is flowed across the heat exchanger manifold. The heat exchanger manifold temperature was maintained at 480–510° C.

Table 1. Minimum Detection Limits for the Possible Decomposition Products of Interest

Species	Concentration (ppm)
HF	0.75
HBr	4.0
CF ₂ O	0.27
CO	0.74
CH ₄	0.12
C ₂ H ₂	0.11
C ₂ H ₄	0.52
HCl	0.82

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